Hydrothermal Crystal Synthesis in the $Ho_2O_3(Yb_2O_3)$–GeO_2–KF–H_2O Systems*

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Crystallization in the $Ho_2O_3(Yb_2O_3)$–GeO_2–KF–H_2O systems has been investigated under hydrothermal conditions. Crystallization fields of the crystalline phases have been determined. Single crystals of $Ho_2Ge_2O_7$, $Yb_2Ge_2O_7$ (two types), K_2HoF_5, K_2YbF_5, $K_xYb_yGe_pO_q$ (P-type), $Ho(OH)_3$, $Yb(OH)_3$, and $K_2Ge_4O_9$ have been obtained. The germanates synthesized have been studied by X-ray analysis and infrared-spectroscopy. Diorthogermanate $Yb_2Ge_2O_7$ has been found to crystallize in two structural types; the first is characterized by the usual structure that is typical for rare-earth germanates, the second is new for germanates of rare-earth elements. High chemical resistance is typical of these crystals. The P-type germanate also has a new type of structure among rare earth germanates. Some suggestions are made as to the structure of these new germanates on the basis of X-ray and ir-spectroscopic data.

Introduction

Preferential incorporation of solvent cation (or anion) into the composition of solid state reaction products is characteristic of crystallization in the majority of germanate and silicate systems. This can be explained by chemical activity of the solvent, NaOH, that is generally used as well as by geometrical correspondence of the structural groupings that are formed. In this paper we show the role of another solvent, KF, in crystallization in complex four-component systems that contain oxides of holmium (or ytterbium) and germanium. As a continuation of references (*1, 2*), this work aimed at obtaining new germanates of the rare earth elements and at showing the basic regularities of phase formation in complex four-component systems and the role of the mineralizer in the process of hydrothermal crystal synthesis.

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Experimental Procedure

Synthesis of the germanates of the rare-earth metals was accomplished by a direct temperature-gradient method. The apparatus and technique for the experiment have been described in detail previously (*3*). A mechanical mixture of the chemical reagents, RE_2O_3 (RE = rare earth) and GeO_2 (hexagonal modification), served as starting material. The variable parameters of the experiment were: C_{KF}, the weight percent concentration of the solvent KF, and N, the mole ratio of the oxides RE_2O_3/GeO_2 in the starting material. The value of N was changed over the interval from 2 to 0.17; the concentration of KF from 0 to 65% by weight. The concentration of the solvent was determined from the density value of the KF solutions at 20°C. The temperature of the dissolution zone was 500°C; the temperature gradient, 2°C/cm (on the outer wall of the autoclave).

The solid state products of the high temperature chemical reaction were studied by

chemical, X-ray, and spectroscopic analyses. Unit cell parameters of the synthesized crystals were evaluated by a photographic X-ray method (using an RKOP camera and molybdenum-filtered radiation).

Results

The Ho_2O_3–GeO_2–KF–H_2O System

The results of the experimental investigation are shown in Fig. 1a in the form of an N vs C diagram. The relative simplicity of the diagram should be noted. There was but one rare-earth germanate detected ($Ho_2Ge_2O_7$) in the entire field of N vs C that was studied. In addition to this germanate, K_2HoF_5, $K_2Ge_4O_9$, $Ho(OH)_3$, and the tetragonal modification of GeO_2 were obtained in the system. A short description of the compounds synthesized is given below.

The *diorthogermanate* $Ho_2Ge_2O_7$ crystallizes in the form of tetragonal plates up to $1 \times 1 \times 0.5$ mm^3 in size (Fig. 2a). The most frequently formed faces were the tetragonal prism {100}, the pinacoid {001}, and the tetragonal bipyramid {114} and {332} (Table I). The crystals were colored green as is characteristic of Ho^{3+} compounds. Unit cell parameters of $Ho_2Ge_2O_7$, as well as of the crystals examined below, are presented in Table II.

The values of the parameters for the holmium diorthogermanate cell are close to those published previously (*4*).

The *crystals of K_2HoF_5* are characterized by prismatic habit elongated along the c axis. The size of the crystals is $10 \times 2 \times 3$ mm^3; the color is light green. The common crystallographic forms are pinacoids {100} and {010}, rhombic prisms {110} and {011}, and rhombic pyramid {111}.

The *tetragermanate $K_2Ge_4O_9$* crystallizes in the form of colorless hexagonal prisms up to $5 \times 4 \times 4$ mm^3 in size. The basic crystalline forms are the hexagonal prism {1010} and the pinacoid {0001}.

The *crystals of $Ho(OH)_3$* have prismatic habit. The crystal size is $10 \times 1.5 \times 1.5$ mm^3. The color is green.

Germanium dioxide, GeO_2 exists in the system in the form of crystals smaller than 0.05 mm. X-rays confirm that it belongs to the tetragonal system.

The Yb_2O_3–GeO_2–KF–H_2O System

The crystallization phase diagram is shown in Fig. 1b. Three ytterbium germanates are synthesized in the system: $Yb_2Ge_2O_7$(I), isostructural with the holmium germanate; $Yb_2Ge_2O_7$ (*F*-type); and $K_xYb_yGe_pO_q$ (*P*-type). Other phases are analogous to those examined for the holmium system.
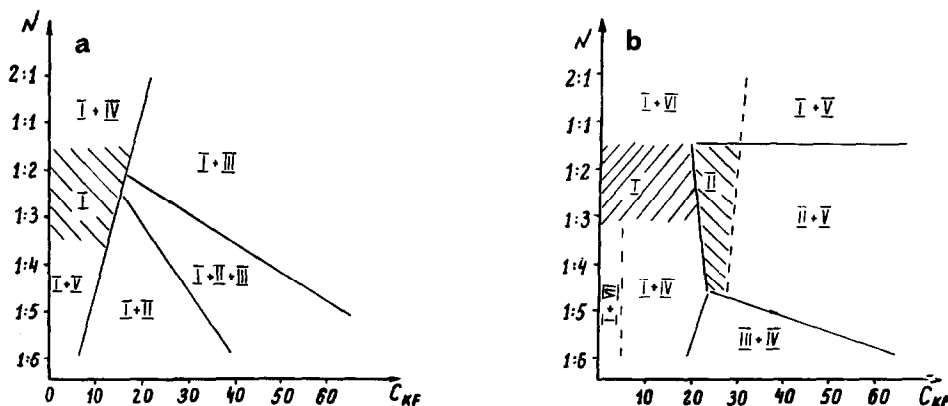

FIG. 1. N vs C diagram of crystallization fields. N is the mole ratio RE_2O_3/GeO_2, C is weight % concentration of solvent KF. (a) Ho_2O_3–GeO_2–KF–H_2O system. Phase designations are: I-$Ho_2Ge_2O_7$, II-$K_2Ge_4O_9$, III-K_2HoF_5, IV-$Ho(OH)_3$, V-GeO_2. Cross-hatched region corresponds to monomineral crystallization. (b) Yb_2O_3–GeO_2–KF–H_2O system. Phase designations are: I-$Yb_2Ge_2O_7$, II-F-type, III-P-type, IV-$K_2Ge_4O_9$, V-K_2YbF_6, VI-$Yb(OH)_3$, VII-GeO_2.
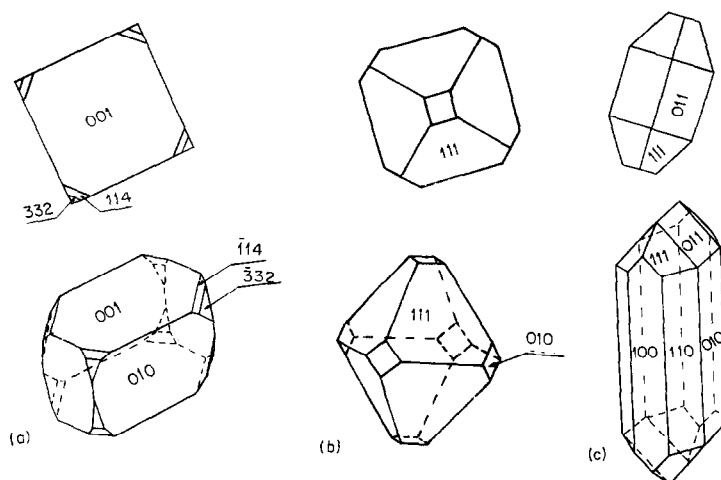
FIG. 2. Common crystal forms: (a) $Ho_2Ge_2O_7$, (b) $Yb_2Ge_2O_7$ (F-type), (c) K_2YbF_5.

TABLE I

RESULTS OF GONIOMETRIC MEASUREMENTS

	$Ho_2Ge_2O_7$			K_2YbF_5			$Yb_2Ge_2O_y$ (F-type)	
$h\,k\,l$	ρ	φ	$h\,k\,l$	ρ	φ	$h\,k\,l$	ρ	φ
1 0 0	90°	90°10′	1 0 0	90°	89°34′	1 0 0	90°	90°
0 0 1	0°		0 1 0	90°	0°	1 1 1	54°44′	45°
1 1 4	33°50′	46°10′	1 1 0	90°	31°20′			
3 3 2	75°04′	45°25′	0 1 1	47°53′	358°			
			1 1 1	52°11′	30°55′			

TABLE II

SYMMETRY AND UNIT CELL PARAMETERS OF THE COMPOUNDS
SYNTHESIZED

Chemical formula	a (Å)	b (Å)	c (Å)	Angle	Cell type, Laue class
$K_xYb_yGe_pO_q$ (P-type)	12.1	11.7	8.5	$\gamma = 111°$	$P2/m$
$Ho_2Ge_2O_7$	6.8		12.3		$P4/m$
$Yb_2Ge_2O_7$	6.7		12.2		$P4/m$
$Yb_2Ge_2O_7$ (F-type)	9.8				$Fm3m$
K_2YbF_5	10.8	6.6	7.3		$Immm$
$K_2Ge_4O_9$	11.8		9.7		$P6/mmm$

The $Yb_2Ge_2O_7$(I) crystals are similar to $Ho_2Ge_2O_7$ in crystal forms and size.

The *F-type crystals* are characterized by enhanced chemical resistance and do not dissolve in hot or cold, concentrated or dilute inorganic acids (HCl, HNO_3, H_2SO_4). In comparison with other germanates, they differ in their greater hardness (>7 on Mohs scale). As to chemical compositions, the preliminary formula $Yb_2Ge_2O_7$ has been assigned to the F-type. Data from X-ray analysis (powder method, Si-filtered radiation) are presented in Table III. Indexing of the X-rays indicates that the F-phase belongs to the $Fm3m$ space group. The crystals grow in the form of an ideally bounded cubooctahedron (Fig. 2b); the common crystalline forms are the hexa-hedron {100} and the octahedron {111}. The crystals are colorless and transparent, the size is $1 \times 1 \times 1$ mm^3. The ir spectrum (Fig. 3a) did not allow assignment of the compound obtained to any of the known structural types of rare earth germanates.

The P-type germanate crystallizes in the monoclinic system; the crystals are characterized by prismatic habit with elongation along the c axis. Clusters of individual colorless crystals measuring $2 \times 0.5 \times 0.5$ mm^3 are often formed. According to the powder X-ray data (Table III), the lattice parameters (Table II), and the ir spectrum (Fig. 3b), this compound also does not have any direct structural analog among the known rare-earth germanates and silicates.

TABLE III

VALUES OF INTENSITIES AND INTERPLANAR DISTANCES FOR P-TYPE AND F-TYPE
PHASES

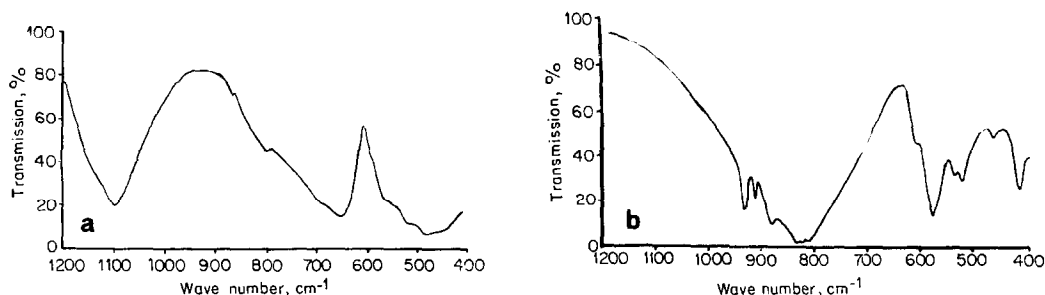| $K_xYb_yGe_pO_q$ (P-type)				$Yb_2Ge_2O_7$ (F-type)		
d/n (Å)	$(I/I_o) \times 100$	d/n (Å)	$(I/I_o) \times 100$	d/n (Å)	$(I/I_o) \times 100$	$h\,k\,l$
5.67	100	2.218	30	5.68	10	1 1 1
5.56	50	2.164	15	2.95	9	3 1 1
5.44	15	2.020	20	2.826	100	2 2 2
4.42	15	1.990	25	2.455	25	4 0 0
4.33	20	1.971	27	2.250	32	3 3 1
4.058	12	1.956	20	1.889	6	3 3 3
3.833	45	1.874	20	1.734	60	4 4 0
3.758	50	1.802	25	1.659	6	5 3 1
3.701	45	1.793	21	1.495	3	5 3 3
3.623	30	1.780	15	1.479	48	6 2 2
3.443	50	1.691	21	1.418	13	4 4 4
3.329	30	1.678	15	1.375	2	7 1 1
3.174	100	1.656	32	1.277	3	7 3 1
3.043	45	1.650	32	1.226	14	8 0 0
3.009	60	1.600	15	1.1990	3	7 3 3
2.926	30	1.574	24	1.1268	33	6 6 2
2.815	65	1.547	22	1.0966	15	8 4 0
2.781	50	1.387	13			
2.663	60	1.383	13			
2.511	45	1.341	15			
2.403	30	1.269	15			
2.333	15	1.187	13			
2.259	15	1.146	10			
2.241	30	1.127	10			

FIG. 3. Infrared spectra of (a) F-type and (b) P-type germanates.

The K_2YbF_5 crystals grow in the form of well-defined colorless prisms up to $10 \times 2 \times 2$ mm^3 in size. The common forms are: pinacoids {100} and {010}, rhombic pyramid {111}, and rhombic prisms {110} and {011} (Fig. 2b).

Discussion

Characteristic of the N vs C diagram for crystallization in the holmium system is a narrow zone of monomineral formation of the rare earth germanate $Ho_2Ge_2O_7$, the only one formed in this system. This zone is situated in the left part of the diagram where there is a slight excess of GeO_2 in the starting material and where the concentrations of KF are less than 10–20%. With further increase in concentration, crystallization of the holmium diorthogermanate is accompanied by precipitation of the fluoride K_2HoF_5. The latter is formed over a broad range of solvent concentrations (up to 65%) and of values of N. With an appreciable excess of germanium, the tetragermanate of potassium $K_2Ge_4O_9$ is also formed. In weakly concentrated solutions excess of one of the components is realized in formation of the trihydroxide $Ho(OH)_3$ and the oxide GeO_2 in tetragonal modification.

The outer areas of the N vs C diagram for the ytterbium system are similar to those for holmium: at small concentrations of KF and insignificant excess of germanium ($N \simeq 0.5$–0.3), there crystallizes the diorthogermanate $Yb_2Ge_2O_7$, which is isostructural with $Ho_2Ge_2O_7$; at high concentrations of mineralizer, there is formed the fluoride K_2YbF_5; other phases [$Yb(OH)_3$ and GeO_2] are analogous to

those found in the Ho system. The basic difference is in the central part of the diagram: there are formed in the system two new types of germanates ($Yb_2Ge_2O_7$, F-type, and $K_xYb_yGe_pO_q$, P-type). On the basis of X-ray analysis and ir-spectroscopic data, one can conclude that these germanates are characterized by new structure types. Consideration of the ir spectra allows us to make some hypotheses about the structure of these compounds. Thus, the presence of a strong absorption in the region of 650 cm^{-1} (Fig. 3a) indicates probable octahedral coordination of Ge in the F-phase structure. At the same time the rather high frequencies, corresponding to deformation vibrations of OGeO (440–570 cm^{-1}), do not exclude the possibility that part of the germanium atoms are in tetrahedral coordination. An intense band appears in the spectrum at 1100 cm^{-1}, which is not at all typical of the ir spectra of germanates that have been previously studied (4). Only for the scandium germanate $Sc_2Ge_2O_7$ was there noted an anomalously high frequency of 1030 cm^{-1}, which corresponds to asymmetric oscillation of the centrosymmetric bridge bond Ge–O–Ge (Ge–O–Ge angle equals 180°).

Among compounds of the type $Me_2^{3+}X_2^{4+}O_7$ where X = Si, Ge, Ti we know only $RE_2Sn_2O_7$ and $RE_2Ti_2O_7$ of the cubic class with unit cell parameters close to the F-type, equal for example, to 10.02 Å for $Yb_2Ti_2O_7$ (5). The crystal structure of cubic titanates, for example $Er_2Ti_2O_7$, has been studied by neutron diffraction (6). The oxytitanium anion is fixed in the structure in the form of an octahedron [TiO_6]. Thus, X-ray and spectroscopic data permit us to formulate a hypothesis about the

possible structural similarity of F-type Yb_2-Ge_2O_7 and cubic titanates $RE_2Ti_2O_7$ (pyrochlore type).

In the spectrum of P-type germanate, there are observed two groups of absorption bands, at 800–900 cm^{-1} and at 460–600 cm^{-1} (Fig. 3b). The second group of bands (460–600 cm^{-1}), corresponding to vibration of the bridge bond Ge–O–Ge (ν_sGeOGe) (4, 7, 8), is characteristic. A similar spectrum is observed in the metagermanate of lead $PbGeO_3$ (if one takes into account that the presence of lead, especially in low coordination number, usually leads to some lowering of the Ge–O vibration frequency), where $PbGeO_3$ is a structural analog of alamosite $PbSiO_3$, in which, according to the data of Ref. (9), there are endless chains of SiO_4 tetrahedra with an identity period of twelve silicon–oxygen tetrahedra. The silicate anion has the

form $[(SiO_3)_{12}]_\infty$. In a centrosymmetric structure only 5 of the 12 vibrations ν_sSiOSi appear active—$3A_u$ and $2B_u$ (this is true for one "molecule" in the unit cell when "Davydov" splitting is absent). If one conjectures in the P-type structure a radical $[(GeO_3)_{12}]_\infty$ (which is entirely probable given the similarity of the spectra of P-type germanate and $PbGeO_3$), then the five absorption bands in the region 450–600 cm^{-1} (Table IV) indicate a centrosymmetric structure as a whole and the presence of Ge–O–Ge bridges with a Ge–O–Ge angle of 180°, confirmed also by the high frequency of some of the vibrations ν_a^s GeOGe (931, 910 cm^{-1}).

Thus, one can hypothesize that the P-type ytterbium germanate is the first rare-earth germanate that has in its structure an anion in the form of an endless chain of germanium–oxygen tetrahedra.

TABLE IV

FREQUENCIES OF MAXIMUM EXTINCTIONS IN THE IR SPECTRA OF F-TYPE AND P-TYPE GERMANATES AND $PbGeO_3$

Assigned vibration	PbGeO$_3$ (9)	P-type	Assigned vibration	F-type
ν_{as}GeOGe ν_{as}GeO$_2$ ν_sGeO$_2$	908 m.[a]	931 m.		1170 sh
	859 s.	910 m.		1140 sh
	850 s.	881 w.		1100 v.s.
	825 sh.	854 sh.		1065 sh.
	798 v.s.	836 v.s.		
	781 v.s.	823 v.s.		
	758 v.s.	808 v.s.		900 v.w.
	748 v.s.			860 v.w.
	725 v.s.		Valence vibration Ge–O	804 v.w.
	712 v.s.			782 v.w.
				685 sh.
				640 v.s.
ν_sGeOGe	578 w.	606 sh.		
	557 s.	574 v.s.		
	524 m.	534 m.		
	511 w.	517 m.	Deformation vibration OGeO νYbO	558 sh.
	470 w.	461 w.		510 sh.
				470 v.s.
δGeO	442 sh.			445
	425 s.			
	415 s.	408 m.		

[a] Notations: w., weak; sh., shoulder; m., medium; s., strong; v.s., very strong.

The results obtained allow us to relate the systems studied to the systems RE$_2$O$_3$–GeO$_2$–KF–H$_2$O (RE = Ho-Lu), which are characterized by a third type of N vs C crystallization diagram. In such systems the diorthogermanates RE$_2$Ge$_2$O$_7$, which crystallize over a broad range of N and C, always predominate.

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